THE PHYSICS OF POLARONS

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INTRODUCTION

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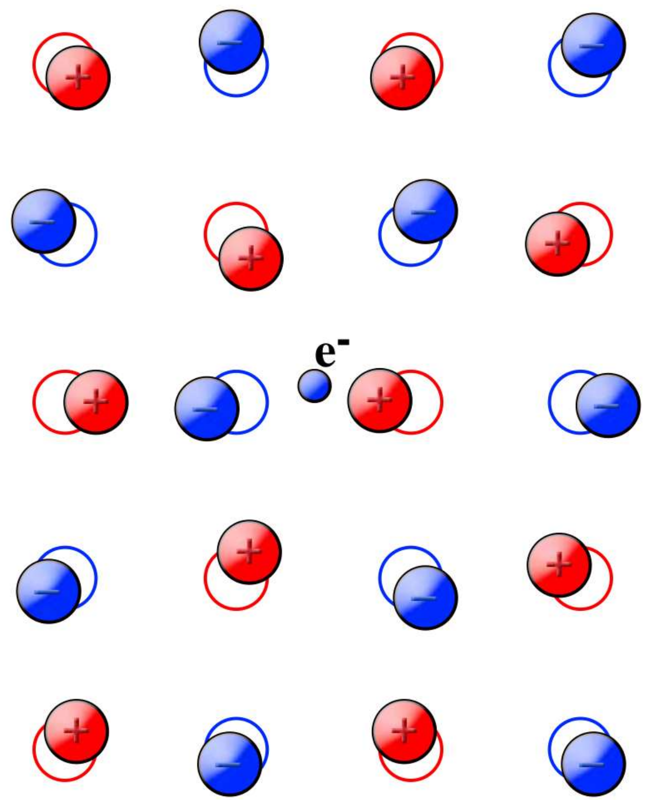
- Polarons: fermionic quasiparticles that form in polarizable materials through the coupling of excess electrons or holes with lattice vibrations (phonons)



HISTORICAL BACKGROUND

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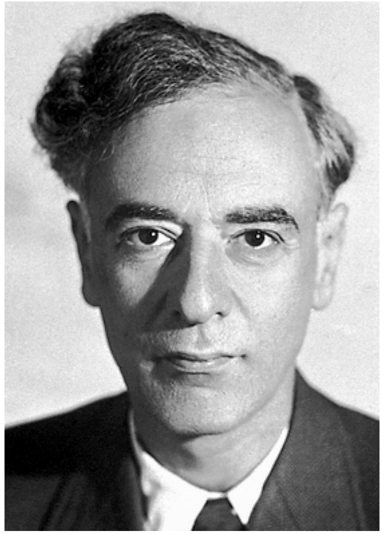
- The polaron concept was proposed by Lev Landau in 1933, and Solomon Pekar in 1946 to describe an electron moving in a dielectric crystal where the atoms displace from their equilibrium positions to effectively screen the charge of an electron, known as a phonon cloud.

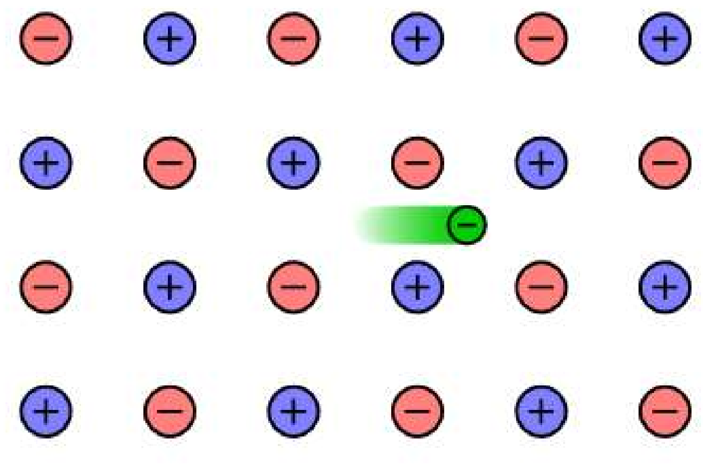


Lev Landau

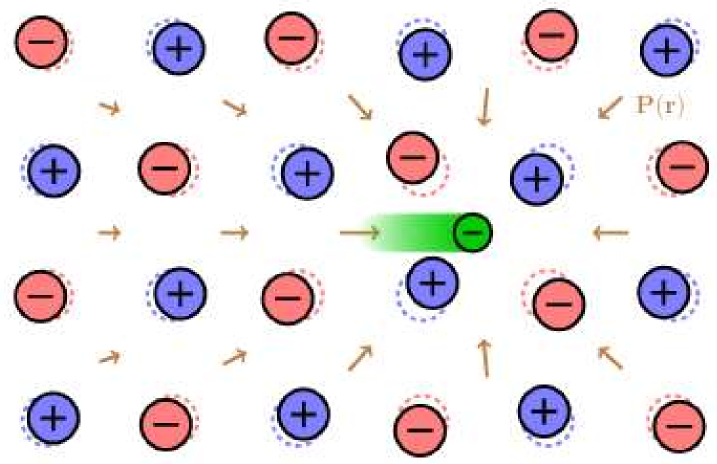
Solomon Pekar

POLARONS

- In the Drude and Sommerfeld models, electrons and ions are treated as independent.
- In reality, electrons (or holes) interact with the lattice, attracting or repelling nearby ions.
- This interaction creates a polarization cloud around the charge carrier, which follows the charge carrier as it propagates through the crystal.



Free electron in the Drude model



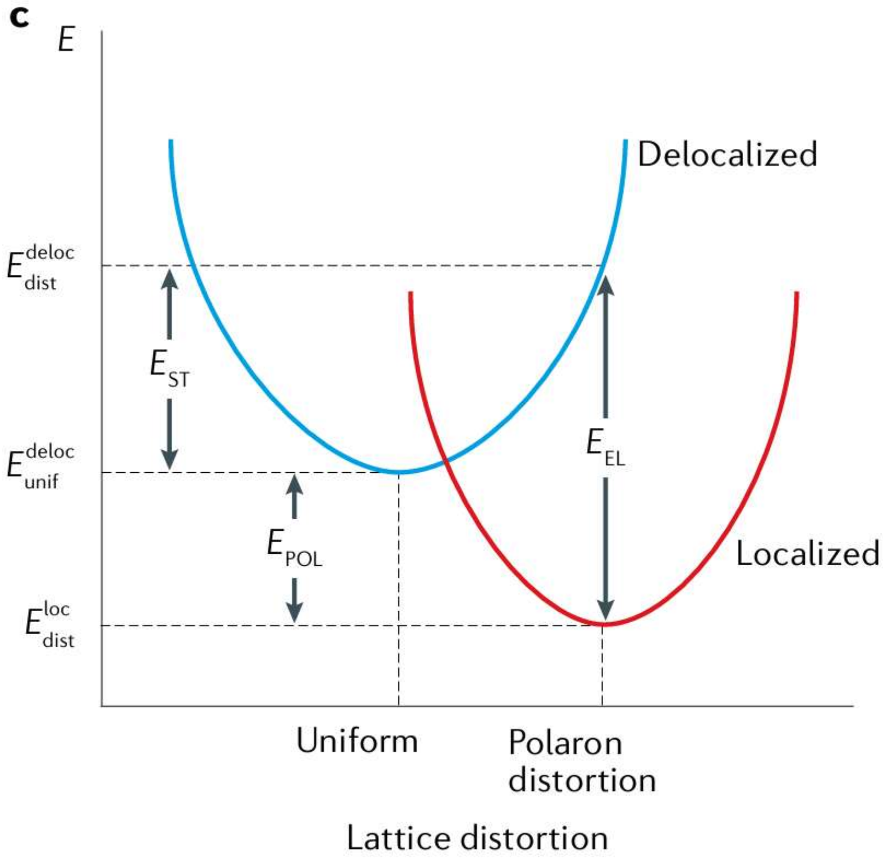
Polaron

PROPERTIES OF POLARONS

I. The electron "dresses" itself with a polarization cloud, leading to a **higher effective mass m***

II. The polaron's interaction with lattice ions creates a self-induced potential well, leading to a **lower energy state** compared to a free electron

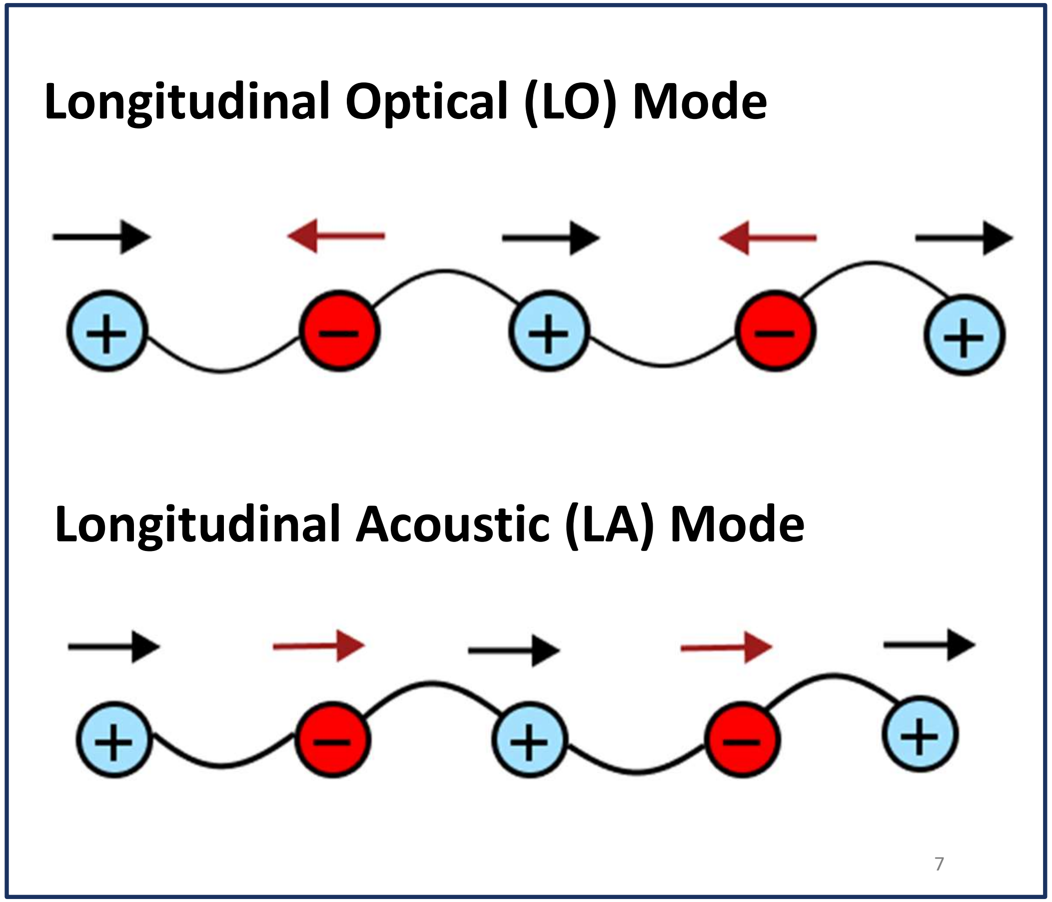
III. The polaron might have a **finite lifetime**



Configuration coordinate diagram depicting the energy balance as a function of lattice distortion for a conduction (delocalized) electron and for a localized polaron.

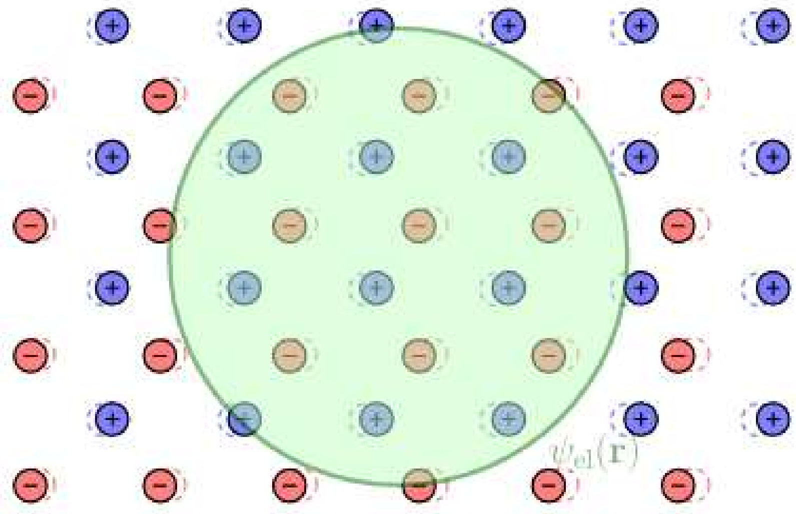
PHONONS

- **Longitudinal optical (LO) phonons** are the primary lattice vibrations that interact with the charge carrier (electron or hole) in a polar crystal, giving rise to a polaron.



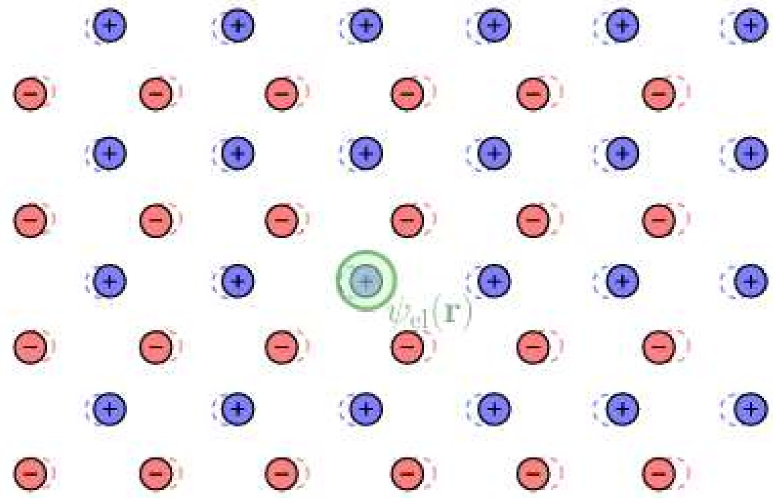
Large Polaron

- Polaron radius ≫ lattice parameter
- Long-range electron–photon interaction
- Coherent motion
- Fröhlich Hamiltonian



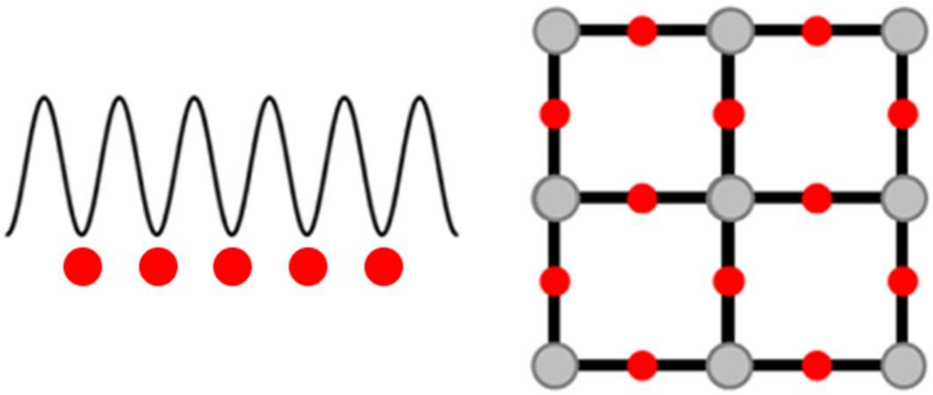
Small Polaron

- Polaron radius ≈ lattice parameter
- Short-range electron–photon interaction
- Phonon-assisted incoherent and diffusive motion (particularly at high temperature)
- Holstein Hamiltonian



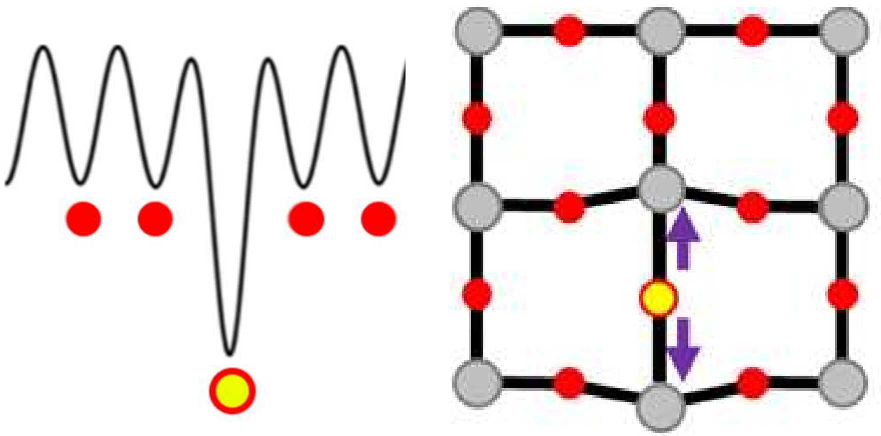
SMALL POLARON

Undistorted lattice



- All the negative sites (red circles) are equivalent, the hole is delocalized.

Self-trapped configuration



- Schematic representation of a small polaron in a crystal: the hole polaron is localized on the yellow atom. It repels the two nearest neighbor atoms, which contribute to stabilize its site.

HOLSTEIN HAMILTONIAN (1959)

$$H = \sum_{n,m,\sigma} t_{n,m} c^{\dagger}_{n,\sigma} c_{m,\sigma} + \hbar \sum_{q} \omega_q b^{\dagger}_q b_q + \frac{g}{\sqrt{N}} \sum_{\mathrm{n},\sigma} c^{\dagger}_{\mathrm{n},\sigma} c_{\mathrm{n},\sigma} \left(b^{\dagger}_n + b_n \right)$$

hopping of the electrons on the lattice

the free phonon Hamiltonian

electron-phonon interaction (g is the short-range electron–phonon coupling term)

Note: c_n and b_q are the annihilation operators for an electron at site n with spin σ and a phonon with wave vector q, respectively.

LARGE POLARON

- Fröhlich formalism in 1954
- Charge carriers in an ionic crystal or a polar semiconductor interact with long-wavelength optical phonons in a polarizable continuum
- Large polarons arise from long-range interactions

FRÖHLICH HAMILTONIAN

$$H = \frac{\hat{\boldsymbol{p}}^2}{2m_b} + \sum_k \hbar\omega_{LO} b_k^+ b_k + \sum_k V_K^F \left(b_K^+ e^{-i\boldsymbol{K}\cdot\boldsymbol{X}} - b_k e^{i\boldsymbol{K}\cdot\boldsymbol{X}}\right)$$

the free electron Hamiltonian

the free phonon Hamiltonian

electron-phonon interaction

$$V_K^F = -i\,\frac{\hbar\omega_{LO}}{k}\sqrt{\frac{4\pi\boldsymbol{\alpha}}{V}}\left(\frac{\hbar}{2m_b\omega_{LO}}\right)^{1/4}$$

Note: The electron (with band mass m_b) is represented in first quantization. The phonons are represented in second quantization, by the the creation and annihilation operators b_k^+ and b_k for longitudinal optical phonons of wave vector k and energy $\hbar\omega_{LO}$.

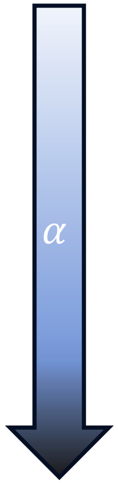
THE FRÖHLICH COUPLING CONSTANT α

3

The long-range electron–phonon coupling V_K^F is characterized by a dimensionless coupling constant α:

$$\alpha = \frac{e^2}{\hbar}\left(\frac{m^*}{2\hbar\omega_{LO}}\right)\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_S}\right)$$

Electron-phonon coupling constants	
Material	$\boldsymbol{\alpha}$
InSb	0.02
GaAs	0.068
AgBr	1.6
KBr	3.05
SrTiO3	4.5



SOLVING THE FRÖHLICH POLARON

3

The Fröhlich Hamiltonian cannot be solved exactly ☹

Lee-Low Pines

Works in the weak coupling regime
($\alpha \ll 1$)

?

Landau-Pekar

Works in the strong coupling regime
($\alpha \gg 1$)

Both models assume that the electron-phonon state factors in two separate WFs: the electron is represented as a wave function that interacts with a classically polarizable continuum (phonons)

α

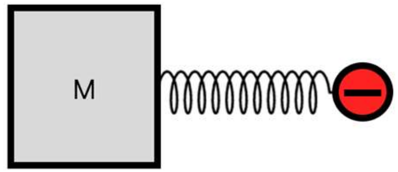
FEYNMAN PATH INTEGRAL APPROACH

Starting Point:

Fröhlich Hamiltonian

$$H = \frac{\hat{P}^2}{2m_b} + \sum_K \hbar\omega_{LO} b_K^+ b_K + \sum_k V_K^F \left(b_K^+ e^{-iK\cdot X} - b_k e^{iK\cdot X}\right)$$

Path Integral Approach



End Result: the most exact variational upper bound for the polaron energy E

$$\mathrm{E} \leq \mathrm{E}_0 + \frac{1}{\hbar}\langle \mathrm{S}_\mathrm{E} - \mathrm{S}_0 \rangle_0$$

S_0: model action of a charge carrier coupled with a cloud of independent phonons through an harmonic interaction

FEYNMAN PATH INTEGRAL APPROACH

1. Start with the Fröhlich Hamiltonian (I) and cast (I) and the Schrödinger Equation (II) into the Lagrangian form of QM

$$H = \frac{\hat{\boldsymbol{P}}^2}{2m_b} + \sum_K \hbar\omega_{LO} b_K^+ b_K + \sum_k V_K^F \left(b_K^+ e^{-i\boldsymbol{K}\cdot\boldsymbol{X}} - b_k e^{i\boldsymbol{K}\cdot\boldsymbol{X}}\right) \text{ (I)} \qquad i\hbar\frac{\partial\psi}{\partial t} = H\psi \text{ (II)}$$

2. Integrate out the field oscillators (phonons) to obtain an effective self-retarded action S_{eff}:

$$S_{eff} = \frac{1}{2}\int\left(\frac{dX}{dt}\right)^2 dt + C\alpha\int\int\frac{\exp(-i|t-s|)}{|\boldsymbol{X_t}-\boldsymbol{X_s}|}dtds$$

FEYNMAN PATH INTEGRAL APPROACH

4

3. Write down the propagator

$$K(X_t, t, X_s, s) = \int_{(X_s, s)}^{(X_t, t)} \mathcal{D}\boldsymbol{X}(\tau) e^{i/\hbar S[X(t)]}$$

4. Introduce the notion of imaginary time $\tau = it$

$$K(X_b, T; X_a, 0) = \int_{(X_a, 0)}^{(X_b, \mathrm{T})} \mathcal{D}\boldsymbol{X}(\tau) e^{-1/\hbar S_E[\boldsymbol{X}(\tau)]}$$

Where $S_E[\boldsymbol{X}(\tau)] := -iS[\boldsymbol{X}(-i\tau)]$ is the Euclidean action functional

WHY IMAGINARY TIME?

Real Time Formulation:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$

$$\psi = \sum_n C_n \varphi_n e^{-\frac{iE_n t}{\hbar}}$$

$$K(X_b, t_b; X_a, t_a) = \int_{(X_a, t_a)}^{(X_b, t_b)} \mathcal{D}\boldsymbol{X}(t) e^{i/\hbar S[\boldsymbol{X}(t)]}$$

Where $S[\boldsymbol{X}(t)]$ is the usual action functional

$$S[\boldsymbol{X}(t)] = \frac{1}{2}\int \left(\frac{d\boldsymbol{X}}{dt}\right)^2 dt + C\alpha \int\int \frac{exp(-i|t-s|)}{|X_t - X_s|} dtds$$

Imaginary Time Formulation:

$$-\hbar \frac{\partial \psi}{\partial \tau} = H\psi$$

$$\psi = \sum_n C_n \varphi_n e^{-\frac{E_n \tau}{\hbar}}$$

$$K(X_b, T; X_a, 0) = \int_{(X_a, 0)}^{(X_b, \mathrm{T})} \mathcal{D}\boldsymbol{X}(\tau) e^{-\frac{1}{\hbar} S_E[\boldsymbol{X}(\tau)]}$$

Where $S_E[\boldsymbol{X}(t)]$ is the Euclidean action functional

$$S_E[\boldsymbol{X}(\tau)] = \frac{1}{2}\int \left(\frac{d\boldsymbol{X}}{d\boldsymbol{t}}\right)^2 d\tau - C\alpha \int\int \frac{exp(-|\tau-\sigma|)}{|X_t - X_s|} d\tau d\sigma$$

FEYNMAN PATH INTEGRAL APPROACH

4. Introduce the notion of imaginary time $\tau = it$ to obtain information about the ground state of a quantum system

$$K(X_b, \mathrm{T}; X_a, 0\,) = \int_{(X_a, 0)}^{(X_b, \mathrm{T})} \mathcal{D}\boldsymbol{X}(\tau) e^{-1/\hbar S_E[\boldsymbol{X}(\tau)]}$$

$$K(X_\tau, \tau; X_\sigma, 0) \sim e^{-\frac{E_0}{\hbar}}$$

5. Estimating the path integral for a large τ gives us the ground-state energy:

$$\mathrm{E}_0 = -\hbar \ln(K)$$

FEYNMAN PATH INTEGRAL APPROACH

Problem: The path integral $K(X_b, T; X_a, 0)$ is not solvable ☹

$$K(X_b, T; X_a, 0) = \int_{(X_a, 0)}^{(X_b, \mathrm{T})} \mathcal{D}\boldsymbol{X}(\tau) e^{-i/\hbar S_E[\boldsymbol{X}(\tau)]}$$

Feynman's Idea: Replace the effective Euclidean action $S_E[\boldsymbol{X}(\tau)]$ with a model action dependent on two model parameters which are varied to minimize the ground-state energy for a given α and LO phonon frequency

Using Jensen-Feynman's inequality:

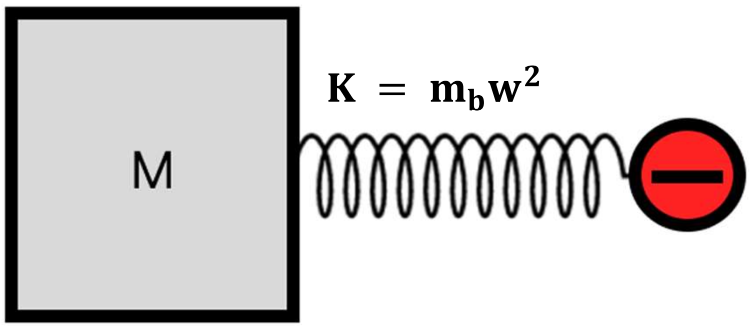
$$\mathrm{E} \leq \mathrm{E}_0 + \frac{1}{\hbar}\langle \mathrm{S}_\mathrm{E} - \mathrm{S}_0 \rangle_0$$

FEYNMAN PATH INTEGRAL APPROACH

4

6. Choose as a model action one where all phonons are replaced by a single mass M, which is harmonically coupled to the electron via a spring with spring constant $K = m_b w^2$

$$S_0 = \frac{1}{2}\int \left(\frac{\mathrm{d}X(\tau)}{\mathrm{d}t}\right)^2 \mathrm{d}\tau + \frac{1}{2}C\int\int [X(\tau) - X(\sigma)]^2 \times \exp(-w|\tau - \sigma|)\mathrm{d}\tau\mathrm{d}\sigma$$



The coupling strength K and w are the variational parameters of the model which are being minimized

SUMMARY

1. $$H = \frac{\widehat{\boldsymbol{P}}^2}{2m_e} + \sum_K \hbar\omega_{LO} b_K^+ b_K + \sum_k V_K^F \left(b_K^+ e^{-i\boldsymbol{K}\cdot\boldsymbol{X}} - b_k e^{i\boldsymbol{K}\cdot\boldsymbol{X}} \right)$$

Fröhlich Hamiltonian

2. $$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$ $$\psi=\sum_n C_n\varphi_n e^{-i\ {}_n t}$$

Introduce the notion of imaginary time $\tau = it$

3. $$K_0 = \int \mathcal{D}\boldsymbol{X}(\tau) e^{-\frac{1}{\hbar}S_0[\boldsymbol{X}(\tau)]}$$ (solvable ☺)

Imaginary path integral using the quadratic model action S_0

4. $$E_0 = -\hbar \ln(K_o)$$ $$\mathrm{E} \leq \mathrm{E}_0 + \frac{1}{\hbar}\langle \mathrm{S_E} - \mathrm{S_0} \rangle_0$$

Jensen-Feynman's inequality to find an upper bound for the true polaron ground state energy

FEYNMAN’S PATH INTEGRAL APPROACH

4

- It provides one of the most accurate analytical approximations for the ground-state energy and effective mass of Fröhlich polarons for all coupling strengths α

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Slow Electrons in a Polar Crystal

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(Received October 19, 1954)

WHY STUDY POLARONS?

- Polarons play an important role in understanding charge transport in materials like **hybrid perovskites**, and **organic semiconductors**, which are at the forefront of energy-conversion technologies and optoelectronic applications.
- **Thermoelectric devices**: Electron–phonon coupling and polarons contribute to all parameters relevant for thermoelectric generators, including the Seebeck effect, electrical conductivity and heat conduction.

Crystals of perovskite
"*Wikipedia, The Free Encyclopedia*"

PATH INTEGRAL AND PARTITION FUNCTION

Additional Notes

- Define $\tau = it$, then β is the inverse temperature

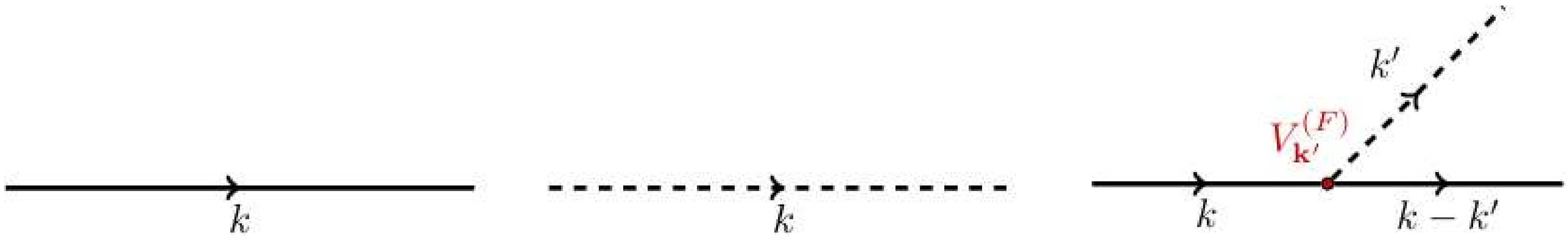
$$K(X_b, \hbar\beta; X_a, 0\,) = \int_{(X_a, 0)}^{(X_b, \hbar\beta)} e^{-1/\hbar S_E[\boldsymbol{X}(\tau)]} \mathcal{D}\boldsymbol{X}(\tau) = \rho(X_\tau, X_\sigma)$$

Several interesting properties of the system can be calculated from the density matrix, but the most important is the partition sum Z:

- $Z = Tr[\rho(X_\tau, X_\sigma)] = \int \rho(r,r) d^3r = \int d^3r_a \int_{(X_a, 0)}^{(X_a, \hbar\beta)} e^{-1/\hbar S_E[\boldsymbol{X}(\tau)]} \mathcal{D}\boldsymbol{X}(\tau)$
- $F = -\frac{1}{\beta}\ln(Z)$ so that at $E_0 = \lim_{\beta\to\infty} -\frac{1}{\beta}\ln(Z)$

FEYNMAN DIAGRAMS FOR THE POLARON PROBLEM

Additional Notes



(a) *Free electron:* $G_0(\mathbf{k}, \omega)$ **(b)** *Free phonon:* $D_0(\mathbf{k}, \omega)$ **(c)** *Fröhlich vertex:* $V_{\mathbf{k}'}^{(F)}$

Figure 2.2. *Different elements that can be used to construct Feynman diagrams for the polaron problem: the Green's functions of the electron and phonon, and the Fröhlich interaction vertex.* $k := (\mathbf{k}, \omega)$ *en* $k' := (\mathbf{k}', \omega')$ *represent four-momenta.*